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A STUDY OF LOW DENSITY, HIGH STRENGTH HIGH MODULUS FILAMENTS AND COMPOSITES

by J. A. Alexander, R. G. Shaver, and J. C. Withers

Prepared by
GENERAL TECHNOLOGIES CORPORATION
Alexandria, Va.
for

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TABLE OF CONTENTS

SUMMARY

This program has been concerned with the fabrication and testing of three types of advanced composite materials:

(1) Metals reinforced with continuous filaments

(2) Metals reinforced with single crystal whiskers

(3) Multilaminar composites consisting of alternate layers of metal and ceramic.

In order to fabricate the filament composites, continuous boron, and batch boron carbide, and silicon carbide filaments were synthesized at GTC.

Electrodeposited nickel was reinforced by both 4 v/o tungsten wire and 20 - 30 v/o boron filament in aligned configuration. Tensile testing of these composites yielded tensile strengths in all cases that exceeded theoretical values calculated by adding the volume-weighted tensile strengths of the components. This effect was most pronounced with the boron filament.

Sapphire whisker composites of powder metallurgically produced Al-6Si matrix and electrodeposited nickel were fabricated and tested. In all cases the whiskers were more or less randomly aligned. Contents up to 16 weight percent whiskers in Al-6Si strengthened the matrix. Approximately 10 weight percent of whiskers in electrodeposited nickel did not strengthen this matrix, although heat treatments did improve the as formed strength.

Work was carried out on the techniques for depositing columbium films and alumina films to form alumina-columbium multilaminar composites. However no composite specimens were fabricated.

I. INTRODUCTION

In response to the ever increasing demands for improved materials to meet the design requirements of advanced space systems, considerable effort is being directed toward the creation of composite materials with properties unavailable in conventional metals and alloys. Filament-reinforced, whisker-reinforced and multi-laminar composites show particular promise for application in the near future. Metal matrix composites of each class have been considered, theoretically and experimentally, in this program.

Filament-reinforced metals yield improved properties by the incorporation of higher strength continuous filaments into a metal matrix. Metal deformation is utilized to distribute the load to the filament and to protect its surface. Whiskers have been grown and tested with extraordinary strengths in the 1 to 3 million psi range. The incorporation of such whiskers into a metal matrix and the full utilization of their available strength offers phenomenal potential. Multilaminar composites on a micro and macro scale offer two different kinds of potential. Thin films, with their whisker-like strengths, might be composited into multilayer structures while maintaining thin film strength. On the other hand thicker metallic layers between brittle ceramics might yield the ductility which has always been lacking in cermet materials.

A metal matrix compositing program is dependent upon the development of new and improved high strength filaments which are more appropriate reinforcements in metal matrices than glass fiber. Thus some effort has been devoted to the production of B, B_4C and SiC filaments for subsequent incorporation into high performance composites. These are the broad dimensions of the program whose results are detailed in this report.

II. FILAMENT REINFORCED COMPOSITES

Glass fiber reinforced plastics are the most well-developed examples of filament reinforced composites. While the strength-to-weight ratio of these composites exceed all other materials, they are useful only for relatively low temperature applications. Filament reinforced metal matrix composites offer the potential of extending the theoretical and technological gains of the glass-plastic composites into a higher temperature realm.

A metal matrix can be reinforced by high strength -high modulus filaments in a manner quite analogous to glass-plastic composites. The ductile metal serves as a surface preservation and stress transfer medium and the high strength-high modulus filaments serve to carry the largest proportion of the load. A desirable metal-matrix-filament reinforced composite should consist of a high strength-high modulus filament embedded in a lower strength-lower modulus metal. The metal matrix should accomplish the transfer of load to the filament via the interfacial bond between them. The continuity of the interfacial bond should be maintained to the point of composite failure. Assuming that the interfacial bond is sufficiently strong, the stress-strain curve for a tensile test of an axially aligned continuous filament composite should exhibit the following sequence of events:

(1) Elastic deformation of both filament and matrix
(2) Elastic deformation of the filament and plastic deformation of the matrix
(3) Plastic deformation of both filament and matrix
(4) Fracture of the filaments
(5) Failure of the matrix

Modifications of this sequence can be expected when, for instance, the elastic portion of the matrix stress-strain curve is essentially non-existent or when the filament fractures with little or no plastic deformation. Interfacial bond failure can likewise be expected to significantly modify the stress-strain behavior.

The bond between filament and matrix need not be a chemical one. Mechanical interlocking or simple friction can provide sufficient strength to accomplish load transfer. Thus topography and morphology of the filament are potentially important to the performance of the composite. Attempts to artificially roughen fiberglass and beryllium filament surfaces have not resulted in better composite performance probably because the character of the etched surface provides notches where stress concentrations result in premature failure.

A. Filament Formation

The reinforcing filaments used in the composites were commercially available tungsten wire and boron filaments which were produced at General Technologies Corporation. In addition to continuous length boron filaments, some one-foot lengths of boron carbide and silicon carbide filaments were produced. The boron filaments were produced by passing BCl_3 and H_2 over a substrate of heated 1/2 mil tungsten wire. Continuous filaments were produced by continuously moving the 1/2 mil wire substrate from a spool through mercury electrodes and winding the boron filament on a spool. The boron was built-up to a total diameter of approximately 4 mils. The initial filaments produced had tensile strengths that varied from 100,000 psi to 225,000 psi. Process development experience resulted in the production of individual runs with strengths ranging from 300,000 psi to 500,000 psi. The range of tensile strength variation in a given run was approximately 20%. The strength of most filament was in the range of 325,000 to 400,000 psi with a density of 2.8 g/cc and a modulus of elasticity of 55×10^6 to 60×10^6 psi. The density of pure boron is 2.3 g/cc. The additional 0.5 g/cc is contributed by the tungsten core.

The boron carbide and silicon carbide filaments were made by the same procedures used to make filaments in Contract NAS 1-2901-S/M which was hydrogen reduction of

BCl_3 in a toluene atmosphere to form B_4C, and $HSiCl_3$ in a toluene atmosphere to produce SiC. Only a few batches of one foot lengths were made. The properties of these filaments are listed as the following:

Property	SiC	B_4C
Density	2.6 g/cc	3.23 g/cc
Flexure Modulus	$20\text{-}80 \times 10^6$ psi	40×10^6 psi
Tensile Strength	<100,000 psi	<100,000 psi

B. Filament Composite Preparation

The winding techniques for fabricating composite components of complex geometry from continuous glass filament and liquid resins has resulted in wide application for glass-plastic composites. Similar flexibility is desirable for metal matrix filament reinforced composites.

A continuous filament winding fabrication technique has been developed at the General Technologies Corporation for metal matrix-filament reinforced composites, and has been used in this program.

The process consists of winding a filament on a preformed mandrel and at the same time electrodepositing, vapor depositing, vacuum depositing or spraying the metal matrix. The vapor and electrodepositing techniques will henceforth be referred to as molecular forming. Initially, tungsten filaments in copper and glass filaments in nickel composites were made to demonstrate that a fully dense composite could be made by simultaneously winding the filament and molecularly forming the metal matrix. Composites having potential practicability such as tungsten or boron filaments in a nickel matrix were then made and their tensile strengths measured.

The composites were made by utilizing a modified lathe as a winding machine and winding the filaments on a stainless steel mandrel while electrodepositing the nickel

matrix. The limited time permitted only a few composites to be made so far. Figures 1 and 2 show cross sections of tungsten and boron filament-nickel matrix composites. The physical properties of composites produced are shown in Table I.

TABLE I

Matrix	Reinforcement	Reinforcement Tensile Strength	Volume % Reinforcement in Matrix	Composite Tensile Strength	Composite Efficiency
Nickel	---	---	--	100-125 x 10^3psi	--
Nickel	1 mil tungsten wire	410,000	4	154 x 10^3psi	110%
Nickel	4 mil boron	500,000	25	300 x 10^3psi	135%
Nickel	4 mil boron	340,000	20	175 x 10^3psi	117%
Nickel	4 mil boron	340,000	30	203 x 10^3psi	117%

The composite efficiencies are calculated based on the tensile strengths predicted by the volume-weighted stress rule verified for tungsten-copper composites by McDanel, et al.(1)

$$S_c = S_f V_f + \sigma^* (1 - V_f)$$

where:

S_c = composite ultimate strength

S_f = filament ultimate strength

σ^* = tensile stress in matrix corresponding to ultimate strain in filaments

V_f = volume fraction of filament

The tungsten wire-nickel composites seem to follow this rule within the accuracy of

(1) McDanels, D. L., Jech, R. W., and Weeton, J. W., "Stress-Strain Behavior of Tungsten-Fiber-Reinforced Copper Composites", NASA TN D 1881, Oct. 1963.

Figure 1. Cross Section of One-Mil Tungsten Wire in Nickel Matrix (400X)

Figure 2. Cross Section of Boron Filament in a Nickel Matrix (200X)

these results. However, this computation of composite strength does not adequately explain the performance of the boron filament nickel composites tested. In these cases the composite tensile strength efficiencies exceed theoretical by 17 to 35%. This is equivalent to saying that the composite strength significantly exceeds the sum of the strengths of the components tested separately in parallel.

The coefficients of variation for the two batches of boron filaments used were 19% and 12%. Coleman[(2)] has analysed the effect of a dispersion of strength upon the strength efficiency of a bundle of filaments and finds that for a coefficient of variation of 10 to 20% the strength efficiency should drop to $\approx 70\%$. Thus the theoretical values presented in Table I are higher than should be expected for composites of continuous filaments having a high coefficient of variation embedded in a metal matrix.

The observation that composite strengths exceed theoretical values may be attributed to two kinds of effects. First the nature of the boron filament surface with its highly irregular "corn cob" nodular structure can be considered to be a multiple notched specimen. When tested as a monofilament these notches act as stress concentrators and result in failure at a stress which is less than could be expected for a perfectly smooth filament. However, when such a filament is embedded by a molecular forming technique, the matrix fills these notches. The applied load is distributed over the contours of the surface reducing the intensity of the stress concentration. Thus, the strength of the embedded filament can be expected to increase toward the value which

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(2) Coleman, B. D., Journal of Mechanics and Physics of Solids, 1958 7, 660.

would be characteristic of a smooth notch-free filament.

The importance of initial flaws to the measured strength of monofilaments has been emphasized by Bradstreet [(3)]. The calculation of the theoretical strength used in Table 1 involves monofilament tensile strength data which is sensitive to the presence of critical flaws. The same continuous filament when embedded in a metal matrix could fail at the same stress and leave two segments of higher strength and of sufficient length to still function effectively as a reinforcing fiber. Thus the strength of the composite would be greater than theoretically calculated because while a failure in a monofilament is catastrophic, in a composite it may simply increase the strength of two fibers which can continue to reinforce the matrix effectively.

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(3) Bradstreet, S. W., "Principles Affecting High Strength to Density Composites with Fibers and Flakes", AD 603308, May 1964.

III. WHISKER REINFORCED COMPOSITES

The unusually high strengths that have been obtained in sapphire and silicon carbide whiskers can revolutionize the development of new composite materials. Tensile strengths of 1 to 3 x 10^6 psi and moduli of 100-300 x 10^6 psi are achieved in production runs of sapphire whiskers produced at Thermokinetic Fibers Inc. and 1 to 3 x 10^6 psi in tensile strength and 100-150 x 10^6 psi in modulus were achieved for SiC whiskers. Both these whisker materials as well as lower grade whiskers with lower physical properties are commercially available.

Because of the extremely fine sizes of the whisker materials new methods have to be developed for handling, processing, orienting and making whiskers-metal matrix composites. Many of the fundamental concepts discussed in the previous section on filament composites are applicable to whisker composites. The only difference is that whiskers are very short when compared to continuous filaments. Strengthening is based on the principle that a ductile matrix can transfer an applied load to short fibers by shear forces at the interface. In such a case the fibers (whiskers) are the principle load-bearing constitutent and the strength of a composite is generally proportional to the whisker content. Thus the strength of a composite will depend on the strength of the whisker and the shear stresses supportable by the whisker metal interface. The shear stresses are a maximum at the middle of the whisker and decreases to a negligible value towards the end. The magnitude of these stresses have been treated in detail by Dow(4). It is evident that if a maximum composite strength is to be achieved, there will be a critical whisker length. The length to diameter ratio of the whisker (aspect ratio)

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(4) Dow, N. F., "Study of Stresses Near Discontinuity in a Filament-Reinforced Composite Metal", Third Report NOw 60-0465d.

determines the magnitude of the average stress being transferred from the matrix to the whisker. The size and geometry of the whisker determines the interfacial area and thus the magnitude of the stress distributed over the whisker. If a whisker is very long compared to its diameter (high aspect ratio) it will act essentially as a continuous filament and thereby the load is carried mainly by the whiskers, but as the length decreases compared to the diameter (low aspect ratio) the proportion of load carried by the whisker decreases and results in a weaker composite. This assumes that good bonding between the matrix and whisker is achieved which permits effective load transfer. Good bonding between the matrix and whiskers, which is frequently referred to as wetting of the whisker by the matrix, is one of the current major problems of achieving efficient high performance whisker composites. Sutton and Chorne[5] have discussed a number of important factors such as this in achieving high strength whisker composites.

A. Whisker Composite Preparation

Because of the very small size of whiskers and their brittleness, extreme care must be taken in fabricating composites to avoid damaging the whiskers, and thereby reducing their aspect ratio. The majority of past works on whisker composites have used liquid infiltration as the fabrication technique. In this study a deposition process and a standard metallurgical hot pressing process were used as the fabrication techniques. Electrodeposition was used to produce a nickel matrix and hot pressing was used to produce an Al-6% Si matrix.

B. Aluminum Alloy-Whisker Composites

The aluminum alloy-whisker composites were produced by mixing aluminum powder,

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(5) Sutton, W. H. & Chorne, J., Metals Engineering Quarterly, Feb. 1963, Vol. 3, No. 1.

silicon powder and TKF 3B loose sapphire whiskers* in isopropyl alcohol in a high speed blender for 5 to 10 seconds. The mixture was dried in an oven at 110°C and then introduced into a mold in the shape of a tensile specimen. The specimens were sheet-type tensile specimens with a one inch gauge length. The mixtures were cold-pressed to 100,000 psi and then sintered up to 4 hours at temperatures to 660°C. The resultant specimens were of very poor quality, low density and they generally broke during mounting for tensile test.

Specimens were then prepared by hot pressing at 1040°F and 30,000 psi for 1/2 hour. The results of the samples prepared and tested are shown in Table II. Cross sections of two composites are shown in Figures 3 and 4. The measured improvement in tensile strength due to the use of whiskers is small. However when whiskers are randomly oriented in a composite, the proportion of load carried by a whisker is expected to be smaller than in the case of axially aligned fibers.

Since at the present time there is no satisfactory theory for the prediction of the strengths of randomly aligned, short filaments, we made predictions of composite strength based on several assumptions in order to compare to our measured values. If the whiskers are randomly oriented in three dimensions, it was reasoned that only 1/3 of them on the average are effectively in the axis of pull. Since the 3B whiskers have an average aspect ratio of 40/1, which is considerably higher than the minimum aspect ratio for stress transfer, the component of the principal stress resolved along the whisker axes will be effectively borne. Therefore the randomly oriented filaments may act as though 1/3 of the total content were perfectly aligned in the axis of pull, whereas

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* Thermokinetic Fibers, Inc., 3B Sapphire whiskers, 400,000 psi tensile strength

Table II. Aluminum - TKF3B Whisker Composites

Weight percent whiskers	0	8	16
Volume percent whiskers	0	5.5	11.4
Density:			
Measured, g/cc	2.58	2.67	2.70
Theoretical, g/cc	2.68	2.75	2.83
Percent of theoretical	96.1	97.1	95.4
Tensile Strength:			
Measured, psi	19,900 18,800	22,300 20,900 21,500	22,400
Average measured, psi	19,350	21,560	22,400
Theoretical, all whiskers effective(1), psi	---	40,480	62,800
Percent of theoretical	---	53.5	35.7
Theoretical, 1/3 of whiskers effective(1,2), psi	---	25,810	32,400
Percent of theoretical	---	83.5	69.1
Percent strength increase over matrix	---	11.4	15.8

(1) based on simple law of mixtures (volume-weighted tensile strengths), whisker strength 400,000 psi

(2) based also on assumption that randomly oriented whiskers carry stress in the principal axis as if 1/3 of the total content were aligned in that axis

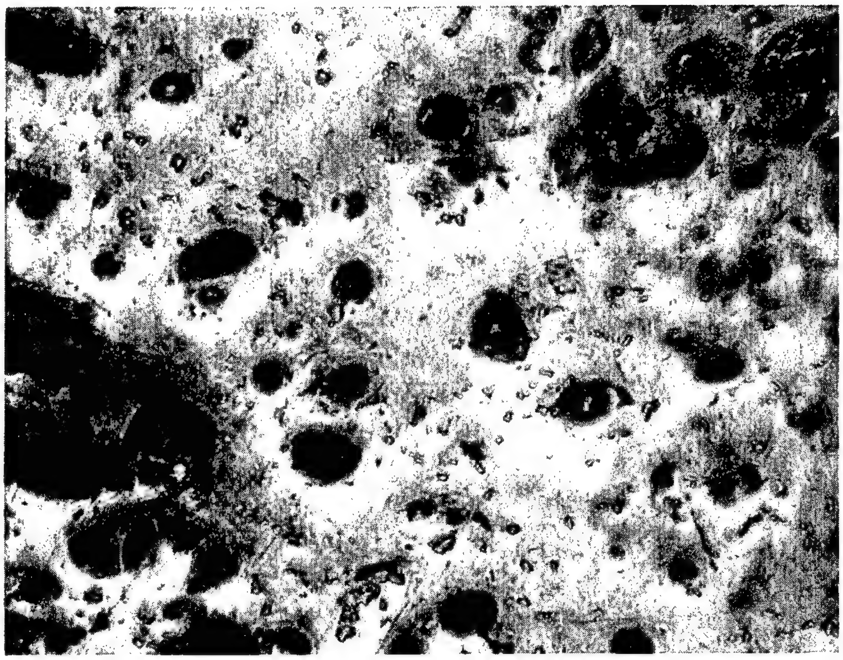

Figure 3. Cross Section of 8 Wt. % Sapphire Whiskers in Al - 6 Si Matrix (200X)

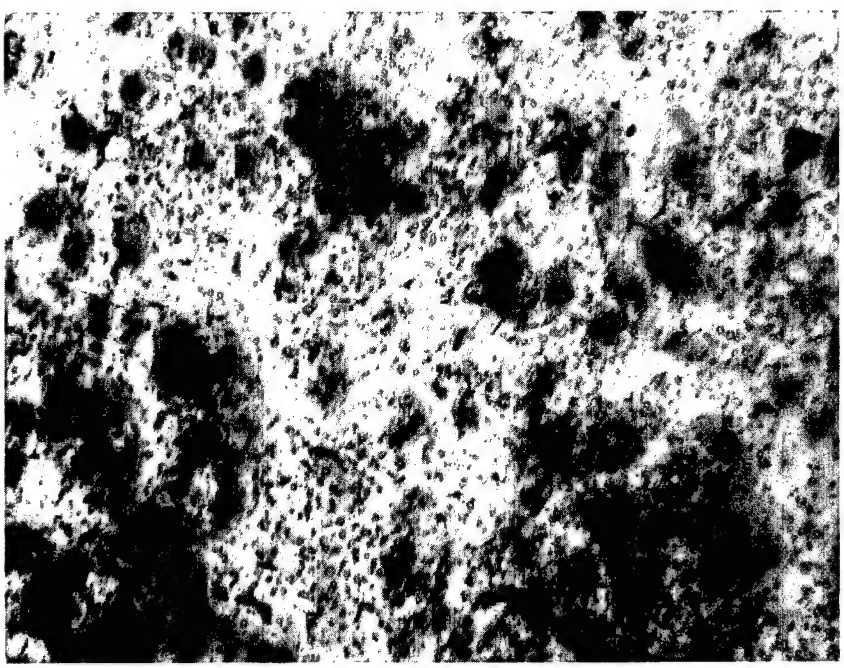

Figure 4. Cross Section of 16 Wt. % Sapphire Whiskers in Al - 6 Si Matrix (200X)

the remainder contribute no strengthening. Theoretical composite strengths were computed on this assumption and are shown in Table II together with theoretical values based on completely aligned filaments and volume-weighted-tensile strengths.

Based on either theoretical strength computation, the composite efficiencies decrease with increasing whisker content, an effect that may or may not be meaningful in view of the simplified composite theory employed. However, if the efficiencies hold for other cases at comparable whisker contents, then the use of prime grade whiskers such as 1A, which has a strength of 1,000,000 to 3,000,000 psi should produce significantly higher strength composites. Improvement in wetting and bonding by coating the whiskers with palladium or nickel, for example, may improve the composite strength, even further.

The alignment of whisker fibers offers a substantial potential for improvement of this type composite. Alighment procedures should be continued to be studied in an effort to regain the 2/3 of whisker strength forfeited in random composites. Additionally, the application of large tensile stresses to the interface between matrix and filament of a poorly aligned filament can result in bond failure. Such bond failure would negate the ability of the whisker to carry the axial component of its applied stress. Thus the simplified estimation of the theoretical strength for these composites may be high depending upon the bond strength at the whisker-metal interface.

C. <u>Nickel-Whisker Composites</u>

Nickel Matrix and sapphire whiskers* were fabricated into composites by two methods. The first consisted of suspending the whiskers in a plating bath and depositing

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* Thermokinetic Fibers, Inc., 3B whiskers

nickel on a copper substrate preshaped for making a tensile specimen. The whiskers were maintained in suspension by continuous agitation. Three specimens having approximately 10 v/o whiskers were made by this method. One was tensile-tested in the as-deposited condition, while another was heat treated at 200°C before testing and the third was heated to 540°C. The tensile strength of the as-deposited composite was 18,000 psi compared to about 100,000 psi for electrodeposited nickel without any whisker content. The tensile strength of the 200°C anneal sample was 20,000 psi, and that of the sample annealed at 540°C was 25,000 psi.

The second method of depositing nickel whisker composites consisted of placing a rectangular cathode in the bottom of the plating container with insulated wires soldered to each end. A rectangular column of plexiglas was constructed the same size as the cathode and raised about 1/8 inch off its surface. Without any bath agitation, whiskers which had been wet with a nickel solution were dropped down the cathode column and settled on the cathode. The whiskers were occluded in the deposit as electrodeposition proceeded. The nickel deposit was cut into three pieces and tested as-deposited and after annealing for one hour at either 800°C or 1000°C. The as-deposited sample broke during mounting and no strength value was obtained. The strength of the annealed samples were 30,000 psi and 80,000 psi for the 800°C and 1000°C anneals, respectively. A cross-section of a composite is shown in Figure 5. These specimens also contained approximately 10 v/o whiskers. A quantative analysis on the specimens was not performed.

The data from these specimens are compared in Table III. As in the Aluminum-whisker composites discussed in the foregoing section, the whiskers in these composites are more or less randomly aligned. In the case of the composites formed by dropping

Figure 5. Cross Section of Randomly Oriented Sapphire Whiskers in Nickel Matrix (400X)

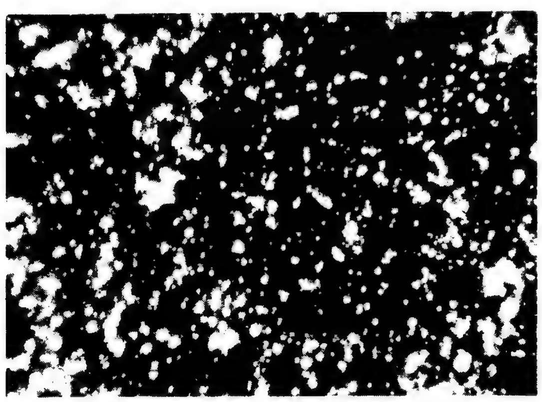

Figure 6. Cross Section of Sapphire Wool Mat in Nickel Matrix (Dark Field) 200X

Table III. Nickel-TKF3B Whisker Composites[a]

Whisker Occlusion Process	Suspended in Plating Bath by Agitation	Dropped upon Horizontal Substrate while Plating
Tensile Strength, psi:		
No anneal	18,000	broke during mounting
Annealed at 200°C	20,000	---
Annealed at 540°C	25,000	---
Annealed at 800°C	---	30,000
Annealed at 1000°C	---	80,000

(a) Electrodeposited nickel has tensile strength of approximately 100,000 psi and 3B whiskers have tensile strength of approximately 400,000 psi.

whiskers through the plating bath upon a substrate, the alignment is probably random within a plane parallel to the tensile test axis. The composites produced by bath agitation should have random whiskers orientation in all planes. The strengths obtained are considerably lower than simple law of mixtures calculations would predict. It is likely that the same general mechanisms of strength degradation are operative in this system as in the aluminum-whisker system; namely, random orientation and lack of good matrix-whisker bond.

The heat treatments probably promoted bonding between the whisker and nickel matrix, which improved the strength of the composites. The use of a higher quality whisker such as TKF No. 1A together with detailed studies of annealing after forming the composite should result in whisker-nickel composites with higher strength at room temperature and good retention of strength at elevated temperatures.

A sapphire whisker paper* was obtained for study. The manufacturer stated that it was made by filtering a suspension of whisker in such a manner that most of the whiskers were oriented in the horizontal plane. The paper is normally 1/8 inch thick and contains 95 to 97% void. Samples of whisker paper were bonded to metal backings and then placed in a nickel plating bath. Deposition occurred from the face of the metal backing and built out through the whisker paper. Voids occurred in some cases but one sample was produced apparently without voids. The sample was not large enough to permit evaluation of physical properties. A cross-section of this specimen is shown in Figure 6.

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* Thermokinetic Fibers, Inc.

IV. LAMINAR COMPOSITES

Laminar composites are of interest because, as with other composites, they may provide properties not available in either component material alone. They have the unique characteristic that each layer may perform a separate and distinct function. For aerospace applications the accomplishment of high strength or rigidity with light weight in thin section are foremost in the list of requirements for such materials. However protection against high temperature oxidation or corrosion resistance or variable thermal and electrical characteristics are feasible in conjunction with strength and rigidity. The possibilities for laminar composites are truly unlimited for while few materials can have all the required characteristics for a specific application, laminar composites can. Design trade off will not be required in their application to high performance hardware.

The tapping of the potential of laminar composites hinges on the ability of the technologist to assemble dissimilar metals, ceramics and inorganics in such a fashion as to utilize the best characteristics of each component. At General Technologies Corporation the processes of vapor, vacuum and electrodeposition are being applied to the construction of laminar composites for study and application. Particular emphasis is being placed on compatible metal-ceramic composites.

A. Theoretical Considerations

Cermets, in the traditional form, have been available for at least fifteen years. Their application has been severely limited by inherent brittleness and low shock resistance. In conventional powder technology cermets, little progress has been made toward the accomplishment of useful ductility in high strength, high temperature

materials. However, Shanley and Knapp[6] have discussed a technique for producing thin layered metal-ceramic composites which provide superior properties if powdered and reconstituted as a cermet.

The principle involved in such property improvement is that closely spaced thin planes of metal are provided to accommodate the applied stress by slip rather than by fracture. The reconstitution of such material provides small elements of laminar structures oriented randomly providing for slip in all directions.

Such composites have been formed by plasma deposition techniques[6] and by the alternate application of a metal and ceramic paint in suspension[7] and improvements in ductility have been claimed. Shevlin[8] has demonstrated a phenomenal increase in toughness, 10 ft lbs to 70 ft. lbs. for Ni lamellae with 90/10% Ti C/Ni without loss of tensile strength. In the excellent 1963 review of metal-ceramic mixtures by Thomas, Huffadine and Moore[9] the authors summarized by saying "If one line of approach only were to be chosen, the authors' own preference would be for fibre-reinforced and laminated cermets. The detail of these topics would necessitate the study of the production and behavior of fibres and lamellae, the interactions between these structural constituents and the matrix, the problems of compatibility, material variability, design, and production."

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(6) F. R. Shanley & W. J. Knapp, Laminated Metal-Ceramic Composite Materials, 6th Sagamore Research Conference, 1959.

(7) W. M. Sterry - Ceramics for Aerospace, Space/Aeronautics, April 1965, Page 53.

(8) T. S. Shevlin, News in Engineering, Volume 31, Page 17, 1959.

(9) A. G. Thomas, J. B. Huffadine & N. C. Moore, Metallurgical Reviews, Vol. 8, Page 461, 1963.

Having at General Technologies Corporation substantial experience in the study of the production and behavior of fibers and fiber-matrix interactions, the study of metal-ceramic lamellae has been undertaker utilizing a combination which should be very compatible, Cb-Al_2O_3. Vapor deposition techniques show promise in controlling or minimizing material variability while maintaining fully dense materials. Such techniques can be adapted to various shapes and can easily be converted from laboratory to production procedures. Another type of laminar composite involves the potential exploitation of the mechanical properties of very thin films. The phenomenal strengths of thin films and whiskers of metals are well documented in the literature. Thin films of metals (<4000° A in thickness) have been observed to have strengths approaching their theoretical strength, E/10.[10,11] Such potential for a materials breakthrough is worthy of exploration, however thin film strength must be maintained at thicker than thin film dimensions to be useful as a structural material.

The most generally accepted explanation for the high strengths exhibited by thin films involves the pinning of dislocations at the two surfaces of the film. As the thickness of film decreases the length of dislocation line is similarly decreased. The stress required to bow out and free such dislocations increases with decrease in the length of a dislocation line. Thus in very thin films little or no plastic deformation occurs until immediately prior to fracture.

Based on this explanation for high strength thin films being valid, thin film strength in greater than thin film thickness should be obtainable by compositing thin

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(10) Beams, J. W., "The Structure and Properties of Thin Films", Wiley & Sons (1959) Page 183.

(11) Menter, J. W. & Pashley, D. W., "The Structures & Properties of Thin Films", Wiley & Sons, Page 119.

films of two or more metals in alternate layers. Such a concept is dependent upon the concurrent maintenance of individual thin film mechanical behavior and adherence at the interface. Similarly the interface should serve as a barrier to dislocation motion from either of the materials. While little has been done experimentally on thin film composites, Weil[12] has reported that a thin film of Ni on iron whiskers doubles their tensile strengths.

B. Laminar Composite Preparation

In order to avoid thermal stresses, we felt that a close match in the coefficients of thermal expansion of the metal and ceramic is desirable. An almost ideal match in expansion is between columbium and Al_2O_3. The vapor deposition of columbium had previously been developed at GTC. The columbium films were deposited by the hydrogen reduction of $CbCl_5$ at 1000°C. A typical deposit was found spectographically to be 99.99+% pure.

The deposition of Al_2O_3 films was investigated from aluminum isopropoxide and the water gas reaction. Aluminum isopropoxide was vaporized over substrates heated from 300 to 900°C. A gray deposit was produced at temperatures above 700°C which was probably contaminated with carbon from breakdown of the organic portion of the moleucle. Good looking deposits were obtained at approximately 500°C at deposition rates of 10 mils/hr. However, the density of the deposits was only 2.8 g/cm^3 compared to 3.9 g/cm^3 for the theoretical density of Al_2O_3. A cross section of the deposit revealed cracks and voids. A few runs have been made at a reduced pressure to improve the density but the density of the deposits was approximately the same as

(12) Weil, I., Journal of Applied Physics, Vol. 30, Page 791, (1959).

those obtained at atmospheric pressure.

A few experiments were run using the water gas reactions:

$$2AlCl_3 + 2CO_2 + 3H_2 \longrightarrow Al_2O_3 + 6HCl + 2CO.$$

The substrate was maintained at 1000°C and a very thin deposit was obtained. The glass chamber walls were covered with powdered Al_2O_3. Difficulty was experienced with vaporizing $AlCl_3$ for longer than a few minutes duration. The surfdce would crust over and vaporization would stop or decrease, then surge and blow the fittings from the vaporizer. It is felt that additional work will yield good films of Al_2O_3 from aluminum isopropoxide or the water gas reaction since only a small effort has been expended in this area with moderate success. No multilaminar composites were made since satisfactory Al_2O_3 films were not deposited.

End

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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